DEVELOPMENT AND OPTIMIZATION OF ZEOLITE SYNTHESIS ROUTE FROM NATURAL KAOLIN FOR ADSORPTION OF DYES

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This thesis is dedicated to all students that have lost their lives in the path of seeking knowledge. May Allah accept your Shahadah.

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ABSTRACT

Synthesis of zeolite using kaolin as the main source of alumina and silica has been identified as a novel zeolite production process, which could reduce the cost of using the synthetic reagents and the high energy consumption. A low grade kaolin was used for studying the most suitable synthesis route and operating parameters for producing a high yield and pure phase zeolite. The study adopted the alkaline activation and microwave assisted heating as modification techniques of the conventional hydrothermal synthesis process. Calcination and crystallization proceses were identified as the bottleneck operations within the process. Hence, this study employed 2^k factorial design of experiment to study the relationship of metakaolinization temperature of 600 – 800 ^oC with calcination time of 1 – 5 hours. And that of crystallization time of 9 – 16 hours with aging treatment time of 12 – 36 hours. Central Composite Design (CCD) is used for optimization with axial and center point for factors evaluation towards the responses; yield percent (%) and crystallinity (%) for crystallization process. Based on the Response Surface Methodology (RSM), with desirability value of 98.67 %, the significant parametric aging condition is 27 hours and crystallization time is 9 hours were suggested to yield an optimum product for 80.47 yield percent and 76.92 crystallinity. Three confirmation runs were performed based on the suggested optimum parameter and the calculated error value was found to be below 10 %. The synthesized zeolite-A from the confirmation runs was characterized through XRD. The results were then corroborated with the analytical results from SEM, BET and FTIR. The activity of the synthesized zeolite A was confirmed by a structural refinement analysis, that identified the product as a member of the cubic crystalline systems, belonging to a Fm3c space group with lattice cubic structure values where: $a = b = c = 24.58$ Å. The synthesized zeolite-A was compared favorably against other low cost adsorbents through its ability to adsorb 2.44 mg/g methylene blue dye at a very low adsorbent medium of 1.5 g/L. The mathematical models suggested by RSM therefore, adequately described the crystallization responses within the zone factors being investigated. It is an outstanding finding to obtain zeolite A, having more than 76% crystallinity, 96.6% phase purity and yielding above 80% from a low grade kaolin and at a considerable low temperature of 90 ^oC and 9 hours crystallization time, without applying any synthetic reagent, as compared to the previous studies that involved the use of expensive and harmful reagents and Structural Directing Agents (SDA) which required longer time and high temperature for crystallization and for post treatment.

ABSTRAK

Sintesis zeolit menggunakan kaolin sebagai sumber utama alumina dan silika telah dikenal pasti sebagai proses pengeluaran zeolit novel, yang dapat mengurangkan kos penggunaan reagen sintetik dan penggunaan tenaga yang tinggi. Kaolin gred rendah telah digunakan untuk menkaji laluan sintesis zeolite yang paling sesuai dan parameter operasi yang sesuai bagi mendapatkan zeolite dengan hasil yang banyak dan berketulenan tinggi. Kajian ini mengadaptasi pengaktifan alkali dan pemanasan gelombang mikro sebagai teknik pengubahsuaian kepada proses sintesis hidroterma konvensional. Proses pengkalsinan dan penghabluran dikenalpasti sebagai operasi penentuan dalam proses tersebut. Oleh itu, kajian ini menggunakan reka bentuk ujikaji faktorik 2k untuk mengkaji interaksi suhu metakaolinisasi 600-800 oC dengan masa pengkalsinan di antara 1-5 jam, masa penghabluran 9-16 jam dengan tempoh pematangan 12-36 jam. Reka bentuk Komposit Sentral digunakan untuk pemodelan dengan titik paksi dan pusat untuk penilaian faktor terhadap respons; peratusan hasil (%) dan penghabluran (%) untuk proses penghabluran. Berdasarkan kaedah permukaan gerak balas (RSM), dengan nilai keinginan 98.67%, keadaan pematangan parametrik yang signifikan ialah 27 jam dan masa penghabluran ialah 9 jam telah dicadangkan untuk menghasilkan produk optimum bagi 80.47 % peratus hasil dan 76.91 % penghabluran. Pengesahan dijalankan sebanyak tiga kali berdasarkan parameter optimum yang disyorkan dan nilai pengiraan kesalahan yang dikira didapati berada di bawah 10 %. Zeolit-A yang disintesis daripada pengujian pengesahan telah dicirikan dan disahkan melalui XRD. Hasilnya disokong dengan hasil analisis dari SEM, BET dan FTIR. Penghasilan sintesis zeolit A yang telah disahkan oleh analisis penyempurnaan struktur, telah dikenalpasti dari ahli sistem hablur kubik, yang dipunyai oleh kumpulan ruang Fm3c dengan struktur nilai kekisi di mana: a = b = c = 24.58 Å. Zeolit-A yang disintesis adalah lebih baik berbanding jenama komersil di pasaran berdasarkan keupayaannya untuk menjerap sebanyak 2.44 mg/g pewarna methalena biru (MB) dengan kuantiti medium bahan serapan yang sangat rendah sebanyak 1.5 g/L. Oleh itu, matematik model yang dicadangkan oleh RSM, secara tepatnya menunjukkan respon penghabluran berada di zon faktor yang dikaji. Ia adalah satu penemuan yang cemerlang untuk mendapatkan zeolit A, mempunyai lebih daripada 76 %penghabluran, fasa ketulenan 96.6 % dan hasil yang melebihi 80 % dari kaolin gred rendah pada suhu yang dikira agak rendah iaitu 90 oC dan masa penghabluran iaitu9 jam, tanpa menggunakan apa-apa bahan tindakbalas sintetik berbanding dengan kajian sebelumnya yang melibatkan penggunaan bahan mahal dan berbahaya dan SDA yang memerlukan masa yang lebih lama dan suhu tinggi untuk penghabluran dan rawatan lanjutan.

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ANOVA	-	Analysis of variance
ASTM	-	American society for testing and materiials
BET		Brunauer–Emmett–Teller
DF	-	Degree of freedom
DGS	-	Dry gel conversion
DOE	-	Design of experiment
ED	-	Electro dialysis
FAU	-	Faujisite topology
FTIR	-	Fourier-transform infrared Spectroscopy
GIS	-	Gismodine
ICDD	-	International centre for diffraction data
ICSD	-	Inorganic Crystal Structure Database.
IZA	-	International zeolite association
LOI	-	Loss on ignition
LTA	-	Linde type Alpha
MB	-	Methylene blue
MED	-	Multiple effect distillation
MOR	-	Mordenite topology
MO	-	Methyl orange
MSF	-	Multi-stage flash distillation
Mt	-	Million ton
O	-	Oxygen
PBU	-	Primary building unit
PRESS	-	Predicted residual error sum of squares
R^2	-	Coefficient of determination
RO	-	Reverse osmosis

RSM	-	Response surface methodology
SAC	-	Steam-assisted crystallization
SBU	-	Secondary building unit
SDA	-	Structural directing agent
SEM	-	Scanning electron microscopy
SOD	-	Sodalite
T	-	Tethrahedral
TEOS	-	Tetraethylorthosilicate
TGA	-	Thermogravimetric analyzer
UTHM	-	Universiti Tun Hussien Onn Malaysia
VCD	-	Vapor compression distillation
VPT	-	Vapor-phase transport
XRD	-	X-ray diffraction
XRF	-	X-ray fluorescence

LIST OF EQUATIONS

REFERENCES

1. Schilling, M., Chiang, L. The effect of natural resources on a sustainable development policy: The approach of non-sustainable externalities. *Energy Policy*. 2011;39(2):990-998.
2. Abdullahi, T., Abdullah, S. S. Sustainability Considerations in Manufacturing and Operation Management. *International Journal of Scientific Engineering and Applied Science.* 2015;1(4):490-497.
3. Malaysia, M. Malaysian Minerals Yearbook. *Minerals and Geoscience Department.* Malaysia. 2012.
4. Atikah, N., Badruddin, M. *Zeolites Catalyst from Oil Palm Ash for Petrochemical Industries*, Degree Thesis. Universiti Malaysia Pahang; 2013.
5. Susilowati, A. *Issues faced in Exporting Zeolite Commodity from Indonesia to Malaysia*. Msc Thesis. Business Management, Asia Pacific University of Technology and Innovation; 2011.
6. Mazur, M., Wheatley, P.S., Navarro, M., Roth, W.J., Položij, M., Mayoral, A., Eliášová, P., Nachtigall, P., Čejka, J. and Morris, R.E. Synthesis of ‘unfeasible’zeolites. *Nature Chemistry*. 2015.
7. Breck, D.W. *Zeolite Molecular Sieves: Structure, Chemistry and Use.* New York.1974.
8. Xu, R., Pang, W., Yu, J., Huo, Q., Chen, J. Chemistry of zeolites and related porous materials: synthesis and structure. *Environmental Engineering and Management* 2008;7(7):73-75.
9. Ajayi, O.A., Abdulkarrem, A., ABO, A., Ityokumbul, S., AM, T., Adefila, S.S. Synthesis of Zeolite ZSM3 from Faujasite: Effects of Post-synthesis Ageing and Insitu seeding. *Synthesis.* 2012;3:29-37.
10. Brooks, W.E. Mineral resource of the month: Arsenic. *Geotimes.* pp. 12 - 16;2008.
11. Kulprathipanja, S. *Zeolites in Industrial Separation and Catalysis.* John Wiley & Sons; 2010.
12. Barrer, R.M. *Hydrothermal Chemistry of Zeolites.* Academic Press; 1982.
13. Meng, X., Xiao, F.S., Green routes for synthesis of zeolites. *Chemical Reviews.* 2013;114(2):1521-1543.
14. McCusker, L., Liebau, F., Engelhardt, G. Nomenclature of structural and compositional characteristics of ordered microporous and mesoporous materials with inorganic hosts (IUPAC Recommendations 2001). *Pure and Applied Chemistry.* 2001;73(2):381-394.

15. Johnson, E., Arshad, S.E. Hydrothermally synthesized zeolites based on kaolinite: A review. *Applied Clay Science.* 2014;97:215-221.

16. Lee, J., Han, S., Hyeon, T., Synthesis of new nanoporous carbon materials using nanostructured silica materials as templates. *Journal of Materials Chemistry*. 2004;14(4):478-486.

17. Yaghi, O.M., O'Keeffe, M., Ockwig, N.W., Chae, H.K., Eddaoudi, M., Kim, J. Reticular synthesis and the design of new materials. *Nature.* 2003;423(6941):705-714.

18. Prasetyoko, D., Ramli, Z., Endud, S., Hamdan, H., Sulikowski, B. Conversion of rice husk ash to zeolite beta. *Waste Management.* 2006;26(10):1173-1179.

19. Chareonpanich, M., Namto, T., Kongkachuichay, P., Limtrakul, J. Synthesis of ZSM-5 zeolite from lignite fly ash and rice husk ash. *Fuel processing Technology*. 2004;85(15):1623-1634.

20. Katsuki, H., Furuta, S., Watari, T., Komarneni, S. ZSM-5 zeolite/porous carbon composite: Conventional-and microwave-hydrothermal synthesis from carbonized rice husk. *Microporous and Mesoporous Materials.* 2005;86(1):145-151.

21. Tanaka, H., Fujii, A. Effect of stirring on the dissolution of coal fly ash and synthesis of pure-form Na-A and-X zeolites by two-step process. *Advanced Powder Technology*. 2009;20(5):473-479.

22. Tanaka, H., Furusawa, S., Hino, R. Synthesis, characterization, and formation process of Na-X zeolite from coal fly ash. *Journal of Materials Synthesis and Processing.* 2002;10(3):143-148.

23. Machado, N.R., Miotto, D.M.M. Synthesis of Na–A and–X zeolites from oil shale ash. *Fuel.* 2005;84(18):2289-2294.

24. Gao, G.M., Zou, H.F., Gan, S.C., Liu, Z.J., An, B.C., Xu, J.J. and Li, G.H. Preparation and properties of silica nanoparticles from oil shale ash. *Powder Technology*. 2009;191(1):47-51.

25. An, B., Wang, W., Ji, G., Gan, S., Gao, G., Xu, J. and Li, G. Preparation of nano-sized α-Al_2O_3 from oil shale ash. *Energy*. 2010;35(1):45-49.

26. Purnomo, C.W., Salim, C., Hinode, H. Synthesis of pure Na–X and Na–A zeolite from bagasse fly ash. *Microporous and Mesoporous Materials.* 2012;162:6-13.

27. Moisés, M.P., da Silva, C.T.P., Meneguin, J.G., Girotto, E.M. Radovanovic, E. Synthesis of zeolite NaA from sugarcane bagasse ash. *Materials Letters.* 2013;108:243-246.

28. Ahmaruzzaman, M. A review on the utilization of fly ash. *Progress in Energy and Combustion Science.* 2010;36(3):327-363.

29. Kazemian, H., Naghdali, Z., Kashani, T.G, Farhadi, F. Conversion of high silicon fly ash to Na-P1 zeolite: Alkaline fusion followed by hydrothermal crystallization. *Advanced Powder Technology*. 2010;21(3):279-283.

30. Wajima, T., Shimizu, T., Ikegami, Y., Synthesis of zeolites from paper sludge ash and their ability to simultaneously remove NH_4^+ and PO_4^{3-}. *Journal of Environmental Science and Health Part A.* 2007;42(3):345-350.

31. Wajima, T., Munakata, K., Material conversion from paper sludge ash in NaOH solution to synthesize adsorbent for removal of Pb^{2+}, NH_4^+ and PO_4^{3-} from aqueous solution. *Journal of Environmental Sciences.* 2011;23(5):718-724.

32. Wajima, T., Munakata, K. Material conversion from waste sandstone cake into cation exchanger using alkali fusion. *Ceramics International.* 2012;38(2):1741-1744.

33. Wajima, T., Munakata, K., Ikegami, Y., Conversion of waste sandstone cake into crystalline zeolite X using alkali fusion. *Materials Transactions.* 2010;51(5):849-854.

34. Wajima, T., Ikegami, Y. Synthesis of crystalline zeolite-13X from waste porcelain using alkali fusion. *Ceramics International.* 2009;35(7):2983-2986.

35. Wajima, T., Ikegami, Y. Zeolitic adsorbent synthesized from powdered waste porcelain, and its capacity for heavy metal removal. *Ars Separatoria Acta.* 2006;4:86-95.

36. Georgiev, D., Bogdanov, B., Hristov, Y., Markovska, I. Synthesis of NaA zeolite from natural kaolinite. *Oxidation Communications.* 2011;34(4):812-819.

37. Covarrubias, C., García, R., Arriagada, R., Yánez, J., Garland, M.T. Cr (III) exchange on zeolites obtained from kaolin and natural mordenite. *Microporous and Mesoporous Materials.* 2006;88(1):220-231.

38. Kovo, A., Hernandez, O., Holmes, S. Synthesis and characterization of zeolite Y and ZSM-5 from Nigerian Ahoko Kaolin using a novel, lower temperature, metakaolinization technique. *Journal of Materials Chemistry.* 2009;19(34):6207-6212.

39. De Lucas, A., Uguina, M.A., Covian, I., Rodriguez, L. Synthesis of 13X zeolite from calcined kaolins and sodium silicate for use in detergents. *Industrial & Engineering Chemistry Research.* 1992;31(9):2134-2140.

40. Youssef, H., Ibrahim, D., Komarneni, S. Microwave-assisted versus conventional synthesis of zeolite A from metakaolinite. *Microporous and Mesoporous Materials.* 2008;115(3):527-534.

41. Jamil, T.S., Youssef, H. Microwave synthesis of zeolites from Egyptian kaolin: Evaluation of heavy metals removal. *Separation Science and Technology.* 2016;51(18):2876-2886.

42. Kovo, A. Effect of temperature on the synthesis of zeolite X from ahoko Nigerian kaolin using novel metakaolinization technique. *Chemical Engineering Communications.* 2012;199(6):786-797.

43. Dion, P., Alcover, J.F., Bergaya, F., Ortega, A. Llewellyn, P. Kinetic study by controlled-transformation rate thermal analysis of the dehydroxylation of kaolinite. *Clay Minerals.* 1998;33(2):269-276.

44. Chin, C.L., Ahmad, Z.A., Sow, S.S. Relationship between the thermal behaviour of the clays and their mineralogical and chemical composition: Example of Ipoh, Kuala Rompin and Mersing (Malaysia). *Applied Clay Science.* 2017;143:327-335.

45. Johnson, E., Arshad, S.E., Asik, J. Hydrothermal synthesis of zeolite A using natural kaolin from KG. gading bongawan sabah. *Journal of Applied Sciences.* 2014;14(23):3282-3289.

46. Abdullah, A.H., Zulkefli, N.N., Aziz, A.S.A., Mat, R. Synthesis of Zeolite Na-A from Local Kaolin for Bioethanol Purification. *Indian Journal of Science and Technology.* 2016;9(9):243-247.

47. Schweiker, G. Sodium silicates and sodium aluminosilicates. *Journal of the American Oil Chemists' Society.* 1978;55(1):36-40.

48. Duan, A., Wan, G., Zhang, Y., Zhao, Z., Jiang, G., Liu, J. Optimal synthesis of micro/mesoporous beta zeolite from kaolin clay and catalytic performance for hydrodesulfurization of diesel. *Catalysis today.* 2011;175(1):485-493.

49. Ríos Reyes, C.A., Williams, C.D., Castellanos Alarcón, O.M. Synthesis of zeolite LTA from thermally treated kaolinite. *Revista Facultad de Ingeniería Universidad de Antioquia.* 2010;2(53):30-41.

50. Subagjo, S., Rahayu, E.S., Samadhi, T.W., Gunawan, M.L. Synthesis of NaY Zeolite Using Mixed Calcined Kaolins. *Journal of Engineering and Technological Sciences.* 2015;47(6):633-639.

51. Abdullahi, T., Harun, Z., Othman, M.H.D. A review on sustainable synthesis of zeolite from kaolinite resources via hydrothermal process. *Advanced Powder Technology.* 2017; 28(8): 1827-1840.

52. Holmes, S.M., Khoo, S.H., Kovo, A.S. The direct conversion of impure natural kaolin into pure zeolite catalysts. *Green Chemistry.* 2011;13(5):1152-1154.

53. Jiang, J., Feng, L., Gu, X. ,Qian, Y., Gu, Y. Duanmu, C. Synthesis of zeolite A from palygorskite via acid activation. *Applied Clay Science.* 2012;55:108-113.

54. Baioumy, H. Mineralogical Variations among the Kaolin Deposits in Malaysia. *Annual International Conference on Geological and Earth Science*; National University of Singapore; 2012. pp.133-140.

55. Musyoka, N.M., Missengue, R., Kusisakana, M., Petrik, L.F. Conversion of South African clays into high quality zeolites. *Applied Clay Science.* 2014;97:182-186.

56. Babalola, R. *Development And Characterization Of Zeolitey From A Nigerian Local Raw Material*, Ph.D. Thesis. Covenant University, Nigeria.; 2015.

57. Johari, I., Said, S., Hisham, B., Bakar, A., Ahmad, Z. Effect of the change of firing temperature on microstructure and physical properties of clay bricks from Beruas (Malaysia). *Science of Sintering.* 2010;42(2):245-254.

58. Byrappa, K., Yoshimura, M. Handbook of Hydrotermal Technology. A Technology for Crystal Growth and Materials Processing. *Byrappa, M Yoshimura-Noyes Publications*, Park Ridge, New Jercy. 2001.

59. Chandrasekhar, S. Influence of metakaolinization temperature on the formation of zeolite 4A from kaolin. *Clay Minerals.* 1996;31(2):253-261.

60. Zones, S.I. Preparation of molecular sieves using a structure directing agent and an N, N, N-trialkyl benzyl quaternary ammonium cation. U.S. Patent and Trademark Office, 2. 2011.

61. Xiao, F.S. *Zeolites in Sustainable Chemistry*, Springer; 2016.

62. Chandrasekhar, S., Pramada, P. Investigation on the synthesis of zeolite NaX from Kerala kaolin. *Journal of Porous Materials.* 1999;6(4):283-297.

63. Petrov, I., Michalev, T. Synthesis of Zeolite A: A Review. *Scientific.* 2012;51(9):30-35.

64. Zimmermann, N.E., Haranczyk, M. History and Utility of Zeolite Framework-Type Discovery from a Data-Science Perspective. *Crystal Growth & Design.* 2016;16(6):3043-3048.

65. Taubert, A., Li, Z. Inorganic materials from ionic liquids. *Dalton Transactions.* 2007(7):723-727.

66. Yasong, W., Yunpeng, X., Zhijian, T., Liwu, L. Research progress in ionothermal synthesis of molecular sieves. *Chinese Journal of Catalysis.* 2012;33(1):39-50.

67. Číčel, B., Novák, I., Horváth, I. Mineralogy and crystallochemistry of clays. *SAV, Bratislava.* 1981.

68. Tschernich, R.W. *Zeolites of the World.* Harbinger House; 1992.

69. Kwakye-Awuah, B., Von-Kiti, E., Nkrumah, I., Williams, C. Towards the Zeolitization of Bauxite: Thermal Behaviour of Gibbsite in High-Alumina-Ghanaian Bauxite. *International Journal of Engineering.* 2013;2(10):1290-1300.

70. Davis, M.E., Lobo, R.F. Zeolite and molecular sieve synthesis. *Chemistry of Materials.* 1992;4(4):756-768.

71. Jacobs, P., Flanigen, E., Jansen, J., van Bekkum, H. Introduction to zeolite science and practice 2nd Ed.: *Elsevier*; 2001.

72. Shoumkova, A. Zeolites for water and wastewater treatment: An overview. *Research Bulletin of the Australian Institute of High Energetic Materials, Special Issue on Global Fresh Water Shortage.* 2011;2:10-70.

73. Georgiev, D., Petrov, I., Mihalev, T., Peychev, I., Gradinarov, I., Kolchakova, G. Granulation of natural zeolite. *Scientific.* 2014;53(10):51-55.

74. Zhicheng, L., Yangdong, W., Zaiku, X. Thoughts on the future development of zeolitic catalysts from an industrial point of view. *Chinese Journal of Catalysis.* 2012;33(1):22-38.

75. Payra, P., Dutta, P.K. Zeolites: A primer. *Handbook of Zeolite Science and Technology.* 2003:1-19.

76. Zheng, N., Bu, X., Wang, B., Feng, P. Microporous and photoluminescent chalcogenide zeolite analogs. *Science.* 2002;298(5602):2366-2369.

77. Baerlocher, C., McCusker, L.B., Olson, D.H. Atlas of zeolite framework types. *Elsevier*; 2007.

78. Gougazeh, M., Buhl, J.C. Synthesis and characterization of zeolite A by hydrothermal transformation of natural Jordanian kaolin. *Journal of the Association of Arab Universities for Basic and Applied Sciences.* 2014;15:35-42.

79. Takaishi, T., Kato, M., Itabashi, K. Determination of the ordered distribution of aluminum atoms in a zeolitic framework. Part II. *Zeolites.* 1995;15(1):21-32.

80. Nozue, Y., Amako, Y., Kawano, R., Mizukane, T., Nakano, T. Insulating state and metallic phase transition of heavily sodium-doped low-silica X (LSX) zeolites. *Journal of Physics and Chemistry of Solids.* 2012;73(12):1538-1541.

81. Petrik, L., Missengue, R., Fatoba, O., Tuffin, M., Sachs, J., Silver/Zeolite Nano Composite-Based Clay Filters For Water Disinfection. *South Africa: Water* Research Commission. 2012.

82. Maesen, T. Chapter 1 - The Zeolite Scene – An Overview. In: Jiří Čejka HvBAC, Ferdi S, eds. *Studies in Surface Science and Catalysis.* Elsevier; Vol 168: pp.1-12; 2007.

83. Lin, J., Dong, Y., Zhang, Q., Hu, D., Li, N., Wang, L., Liu, Y. and Wu, T. Interrupted Chalcogenide-Based Zeolite-Analogue Semiconductor: Atomically Precise Doping for Tunable Electro-/Photoelectrochemical Properties. *Angewandte Chemie.* 2015;127(17):5192-5196.

84. Baerlocher, C., McCusker. L. Database of zeolite structures. iza-structure;2012.

85. Carrondo, M.J., Perry. R., Lester, J.N. Sedimentation of zeolite type A in water and waste water. *Canadian Journal of Civil Engineering.* 1981;8(2):206-217.

86. Mostafa, A., Youssef, H., Sorour, M., Tewfik, S., Shalaan, H. Utilization of Egyptian kaolin for zeolite-A preparation and performance evaluation. Paper presented at: *2nd International Conference on Environmental Science and Technology.* University Malaya. 2011.

87. Cook, T.E., Cilley, W.A., Savitsky, A.C., Wiers, B.H. Zeolite A hydrolysis and degradation. *Environmental Science & Technology.* 1982;16(6):344-350.

88. Kurzendorfer, C.P., Kuhm, P., Steber, J. Zeolites in the environment. *Detergents and the Environment*: CRC Press; 1996:141-208.

89. Melo, C.R., Riella, H.G., Kuhnen, N.C. Synthesis of 4A zeolites from kaolin for obtaining 5A zeolites through ionic exchange for adsorption of arsenic. *Materials Science and Engineering: B.* 2012;177(4):345-349.

90. Ugal, J.R., Hassan, K.H., Ali, I.H. Preparation of type 4A zeolite from Iraqi kaolin: Characterization and properties measurements. *Journal of the*

Association of Arab Universities for Basic and Applied Sciences. 2010;9(1):2-5.

91. Dyer, A. *An Introduction to Zeolite Molecular Sieves*. Science Publishers, Khlimcov,1988.

92. Broach, R.W., Kirchner, R.M. Structures of the K^+ and NH_4^+ forms of Linde J. *Microporous and Mesoporous Materials.* 2011;143(2):398-400.

93. Baerlocher, C., McCusker, L. Database of Zeolite Structures, 2008. *URL http://www iza-structure org/databases.* 2012.

94. Polatoğlu, İ. *Chemical Behaviour of Clinoptilolite rich Natural Zeolite in Aqueous Medium*. Msc Thesis. İzmir Institute of Technology; 2005.

95. Haag, W. Catalysis by zeolites–science and technology. *Studies in Surface Science and Catalysis.* 1994;84:1375-1394.

96. Cejka, J., Van Bekkum, H., Corma, A., Schueth, F. *Introduction to Zeolite Molecular Sieves.* Vol 168: Elsevier; 2007.

97. Zhao, J., Yan, W., Xu, R., Pang, W., Huo, Q. Modern Inorganic Synthetic Chemistry. *Elsevier.* Amsterdam; 2011.

98. Borade, R., Sayari, A., Adnot, A., Kaliaguine, S. Characterization of acidity in ZSM-5 zeolites: an X-ray photoelectron and IR spectroscopy study. *Journal of Physical Chemistry;(USA).* 1990; 94(15).

99. Borges, M., Sierra, M., Cuevas, E., García, R., Esparza, P. Photocatalysis with solar energy: Sunlight-responsive photocatalyst based on TiO_2 loaded on a natural material for wastewater treatment. *Solar Energy.* 2016;135:527-535.

100. Dubey, N., Rayalu, S.S., Labhsetwar, N.K., Naidu, R,R., Chatti, R.V, Devotta, S. Photocatalytic properties of zeolite-based materials for the photoreduction of methyl orange. *Applied Catalysis A: General.* 2006;303(2):152-157.

101. Tedla, H., Díaz, I., Kebede, T., Taddesse, A.M. Synthesis, characterization and photocatalytic activity of zeolite supported $ZnO/Fe_2O_3/MnO_2$ nanocomposites. *Journal of Environmental Chemical Engineering.* 2015;3(3):1586-1591.

102. Worch, E. *Adsorption technology in water treatment: fundamentals, processes, and modeling.* Walter de Gruyter; 2012.

103. Choudhury, T.R., Pathan, K., Amin, M.N., Ali, M., Quraishi, S., Mustafa, A. Adsorption of Cr (III) from aqueous solution by groundnut shell. *J Environ Sci Water Res.* 2012;1(6):144-150.

104. Bousba, S., Meniai, A.H. Removal of phenol from water by adsorption onto sewage sludge based adsorbent. *Chem Eng Trans.* 2014;40.

105. Hamed, M.M., Ahmed, I., Metwally, S. Adsorptive removal of methylene blue as organic pollutant by marble dust as eco-friendly sorbent. *Journal of Industrial and Engineering Chemistry*. 2014;20(4):2370-2377.

106. Cundy, C.S., Cox, P.A. The hydrothermal synthesis of zeolites: history and development from the earliest days to the present time. *Chemical Reviews.* 2003;103(3):663-702.

107. Zimmerman, B.J., Schunk, D.H. *Educational psychology: A century of contributions: A Project of Division 15 (educational Psychology) of the American Psychological Society*. Routledge; 2014.

108. Jentys, A., Lercher, J. Techniques of zeolite characterization. *Studies in Surface Science and Catalysis.* 2001;137:345-386.

109. Julbe, A., Farrusseng, D., Jalibert, J., Mirodatos, C., Guizard, C. Characteristics and performance in the oxidative dehydrogenation of propane of MFI and V-MFI zeolite membranes. *Catalysis Today*. 2000;56(1):199-209.

110. Flanigen, E.M. Zeolites and molecular sieves: An historical perspective. *Studies in Surface Science and Catalysis.* 2001;137:11-35.

111. Akolekar, D., Chaffee, A., Howe, RF. The transformation of kaolin to low-silica X zeolite. *Zeolites.* 1997;19(5):359-365.

112. Alberti, A., Colella, C., Oggiano, G., Pansini, M., Vezzalini, G. Zeolite production from waste kaolin containing materials. *Materials Engineering (Modena, Italy).* 1994;5:145-158.

113. Yu, J. Synthesis of zeolites. *Studies in Surface Science and Catalysis.* 2007;168:39-103.

114. Heller-Kallai, L. Thermally modified clay minerals. *Science Chapters.* 2013;10:411-433.

115. Alkan, M., Hopa, Ç., Yilmaz, Z., Güler, H. The effect of alkali concentration and solid/liquid ratio on the hydrothermal synthesis of zeolite NaA from natural kaolinite. *Microporous and Mesoporous Materials.* 2005;86(1):176-184.

116. Feng, H., Li, C., Shan, H. Effect of calcination temperature of kaolin microspheres on the in situ synthesis of ZSM-5. *Catalysis Letters.* 2009;129(1-2):71-78.

117. Souza, G., Sanchez, R., Holanda, J. Thermal and structural characterization of Brazilian south-eastern kaolinitic clays. *Journal of Thermal Analysis and Calorimetry*. 2003;73(1):293-305.

118. Basaldella, E., Kikot, A., Pereira, E. Synthesis of zeolites from mechanically activated kaolin clays. *Reactivity of Solids.* 1990;8(1-2):169-177.

119. Hubadillah, S.K., Othman, M.H.D., Harun, Z., Ismail, A.F., Iwamoto, Y., Honda, S., Rahman, M.A., Jaafar, J., Gani, P. and Sokri, M.N.M., 2016. Effect of fabrication parameters on physical properties of metakaolin-based ceramic hollow fibre membrane (CHFM). *Ceramics International.* 2016;42(14):15547-15558.

120. Murat, M., Amokrane, A., Bastide, J., Montanaro, L. Synthesis of zeolites from thermally activated kaolinite. Some observations on nucleation and growth. *Clay Minerals.* 1992;27(1):119-130.

121. Ball, W., Dwyer, J., Garforth, A., Smith, W. The Synthesis and Characterisation of Iron Silicate Molecular Sieves Sieves. *Studies in Surface Science and Catalysis.* 1986;28:137-144.

122. Murray, H., Murray, H. Applied Clay Mineralogy: Occurrences. *Processing and Application of Kaolins, Bentonites, Palygorskite-Sepiolite and Common Clays, Elsevier's Science & Technology Right Department in Oxford, UK.* 2007.

123. Shafiq, N., Nuruddin, M.F., Khan, S.U., Ayub, T. Calcined kaolin as cement replacing material and its use in high strength concrete. *Construction and Building Materials.* 2015;81:313-323.

124. Ojha, K., Pradhan, N.C., Samanta, A.N. Zeolite from fly ash: synthesis and characterization. *Bulletin of Materials Science.* 2004;27(6):555-564.

125. Colina, F.G., Llorens, J. Study of the dissolution of dealuminated kaolin in sodium–potassium hydroxide during the gel formation step in zeolite X synthesis. *Microporous and Mesoporous Materials.* 2007;100(1):302-311.

126. Tavasoli, M., Kazemian, H., Sadjadi, S., Tamizifar, M. Synthesis and Characterization of Zeolite NaY Using Kaolin With Different Synthesis Methods. *Clays and Clay Minerals.* 2014;62(6):508-518.

127. Sun, G., Liu, Y., Yang, J., Wang, J. Seeded synthesis of small polycrystalline NaY zeolite membrane using zeolite structure-directing agent and its pervaporation performance. *Journal of Porous Materials.* 2011;18(4):465-473.

128. Mackinnon, I.D., Millar, G.J., Stolz, W. Hydrothermal syntheses of zeolite N from kaolin. *Applied Clay Science.* 2012;58:1-7.

129. Kazemimoghadam, M., Mohammadi, T. Preparation of NaA zeolite membranes for separation of water/UDMH mixtures. *Separation and purification technology*. 2006;47(3):173-178.

130. Hildebrando, E.A., Andrade, C.G.B., Rocha, C.A.F.d, Angélica, R.S., Valenzuela-Diaz, F.R., Neves, R.F. Synthesis and characterization of zeolite NaP using kaolin waste as a source of silicon and aluminum. *Materials Research.* 2014;17:174-179.

131. Chandrasekhar, S., Pramada, P. Microwave assisted synthesis of zeolite A from metakaolin. *Microporous and Mesoporous Materials.* 2008;108(1):152-161.

132. Kovo, A., Holmes, S. Effect of aging on the synthesis of kaolin-based zeolite Y from ahoko Nigeria using a novel metakaolinization technique. *Journal of Dispersion Science and Technology*. 2010;31(4):442-448.

123. Caballero, I., Colina, F.G., Costa, J. Synthesis of X-type zeolite from dealuminated kaolin by reaction with sulfuric acid at high temperature. *Industrial & Engineering Chemistry Research.* 2007;46(4):1029-1038.

134. Zhang, Y., Gao, W., Cui, L. The transformation of acid leached metakaolin to zeolite beta. *Studies in Surface Science and Catalysis.* 2007;170:420-425.

135. Khalil, U., Muraza, O. Microwave-assisted hydrothermal synthesis of mordenite zeolite: Optimization of synthesis parameters. *Microporous and Mesoporous Materials.* 2016;232:211-217.

136. Flanigen, E.M., Broach, R.W., Wilson, S.T. Introduction. *Zeolites in Industrial Separation and Catalysis.* 2010:1-26.

137. Novembre, D., Di Sabatino, B., Gimeno, D., Garcia-Vallès, M., Martinez-Manent, S. Synthesis of Na–X zeolites from tripolaceous deposits (Crotone, Italy) and volcanic zeolitised rocks (Vico volcano, Italy). *Microporous and Mesoporous Materials.* 2004;75(1-2):1-11.

138. Von-Kiti, E. *Synthesis and Characterization of Zeolites from Bauxite and Kaolin: Application to the Removal of Heavy Metals from Mining Wastewater.* PhD Thesis. Kwame Nkrumah University of Science And Technology Kumasi, Ghana; 2017.

139. Noack, M., Kölsch, P., Schäfer, R., Toussaint, P., Caro, J. Molecular sieve membranes for industrial application: problems, progress, solutions. *Chemical Engineering & Technology.* 2002;25(3):221-230.

140. Julbe, A. Zeolite membranes—a short overview. *Studies in Surface Science and Catalysis.* 2005;157:135-160.

141. Freeman, B., Yampolskii, Y., Pinnau, I. *Materials Science of Membranes for Gas and Vapor Separation.* John Wiley & Sons; 2006.

142. Wang, T., Lu, X., Yan, Y. Synthesis, characterization and crystallization mechanism of SAPOs from natural kaolinite. *Microporous and Mesoporous Materials.* 2010;136(1):138-147.

143. Singh, R., Dutta, P.K. MFI: a case study of zeolite synthesis. *Handbook of Zeolite Science and Technology.* 2003;35:21-64.

144. Xu, R., Pang, W., Yu, J., Huo, Q., Chen, J. *Chemistry of Zeolites and Related Porous Materials: Synthesis and Structure.* John Wiley & Sons; 2009.

145. Ko, Y.S., Ahn, W.S. Crystallization of zeolite L from Na_2O–K_2O–Al_2O_3–SiO_2–H_2O system. *Powder technology.* 2004;145(1):10-19.

146. Ciric, J. Kinetics of zeolite A crystallization. *Journal of Colloid and Interface Science.* 1968;28(2):315-324.

147. Kacirek, H., Lechert, H. Rates of crystallization and a model for the growth of sodium-Y zeolites. *The Journal of Physical Chemistry.* 1976;80(12):1291-1296.

148. Zhdanov, S., Samulevich, N. Nucleation and crystal growth of zeolites in crystallizing aluminosilicate gels. Paper presented at: Proceedings of the fifth international conference on zeolites, Naples, Italy1980.

149. Huo, Q., Feng, S., Xu, R. Zeolites: Facts, Figures, Future. In Jacobs, P. A and RA van Santen (Ed). *Zeolite science*. Elsevier; Amsterdam.pp. 23-98; 1989.

150. Huo, Q., Feng, S., Xu, R. Study on the syntheses of silica-zeolites in nonaqueous media-crystallization of silica-sodalite and silica-zsm-39. *Acta Chimica Sinica.* 1990;48(7):639-643.

151. Meng, X., Wang, L., Xiao, F.S. Sustainable Routes for Zeolite Synthesis. *Zeolites in Sustainable Chemistry*: Springer; 2016:3-35.

152. Cooper, E.R., Andrews, C.D., Wheatley, P.S, Webb, P.B., Wormald, P., Morris, R.E. Ionic liquids and eutectic mixtures as solvent and template in synthesis of zeolite analogues. *Nature*. 2004;430(7003):1012.

153. Roth, W.J., Nachtigall, P., Morris, R.E., Wheatley, P.S., Seymour, V.R., Ashbrook, S.E., Chlubná, P., Grajciar, L., Položij, M., Zukal, A. and Shvets, O. A family of zeolites with controlled pore size prepared using a top-down method. *Nature chemistry*. 2013;5(7):628-633.

154. Matsukata, M., Ogura, M., Osaki, T., Rao, P.R.H.P., Nomura, M., Kikuchi, E. Conversion of dry gel to microporous crystals in gas phase. *Topics in Catalysis*. 1999;9(1-2):77-92.

155. Lee, H., Zones, S.I., Davis, M.E. A combustion-free methodology for synthesizing zeolites and zeolite-like materials. *Nature*. 2003;425(6956):385-388.

156. Kingston, H., Haswell, S. Microwave Enhanced Chemistry, Professional Reference Book Series. *American Chemical Society, Washington, DC Leray C, Grcic T, Gutbier G, Bnouham M (1995) Analusis*. 1997;23(65):227.

157. Ryan, M.A., Tinnesand, M. *Introduction to Green Chemistry, Instructional Activities for Introductory Chemistry*. Washington, D. C: American Chemical Society; 2002.

158. Rao, K., Vaidhyanathan, B., Ganguli, M., Ramakrishnan, P. Synthesis of inorganic solids using microwaves. *Chemistry of Materials*. 1999;11(4):882-895.

159. Tompsett, G.A., Conner, W.C., Yngvesson, K.S. Microwave synthesis of nanoporous materials. *ChemPhysChem*. 2006;7(2):296-319.

160. Chon, H., Ihm, S.K., Uh, Y.S. *Progress in Zeolite and Microporous Materials*. Vol 105: Elsevier; 1996.

161. Sathupunya, M., Gulari, E., Wongkasemjit, S. ANA and GIS zeolite synthesis directly from alumatrane and silatrane by sol-gel process and microwave technique. *Journal of the European Ceramic Society*. 2002;22(13):2305-2314.

162. Slangen, P., Jansen, J., Van Bekkum, H. The effect of ageing on the microwave synthesis of zeolite NaA. *Microporous Materials*. 1997;9(5):259-265.

163. Chen, C.S.H., Schlenker, J.L., Wentzek, S.E. Synthesis and characterization of synthetic zeolite ECR-1. *Zeolites*. 1996;17(4):393-400.

164. Sapawe, N., Jalil, A.A., Triwahyono, S., Shah, M.I.A., Jusoh, R., Salleh, N.F.M., Hameed, B.H. and Karim, A.H. Cost-effective microwave rapid synthesis of zeolite NaA for removal of methylene blue. *Chemical Engineering Journal*. 2013;229:388-398.

165. Iqbal, N., Kadir, M.R.A., Mahmood, N.H.B., Yusoff, M.F.M., Siddique, J.A., Salim, N., Froemming, G.R., Sarian, M.N., Raghavendran, H.R.B. and

Kamarul, T. Microwave synthesis, characterization, bioactivity and in vitro biocompatibility of zeolite–hydroxyapatite (Zeo–HA) composite for bone tissue engineering applications. *Ceramics International*. 2014;40(10):16091-16097.

166. Ansari, M., Aroujalian, A., Raisi, A., Dabir, B., Fathizadeh, M. Preparation and characterization of nano-NaX zeolite by microwave assisted hydrothermal method. *Advanced Powder Technology*. 2014;25(2):722-727.

167. Tanaka, H., Fujii, A., Fujimoto, S., Tanaka, Y. Microwave-assisted two-step process for the synthesis of a single-phase Na-A zeolite from coal fly ash. *Advanced Powder Technology*. 2008;19(1):83-94.

168. Zhao, H., Deng, Y., Harsh, J.B., Flury, M., Boyle, J.S. Alteration of kaolinite to cancrinite and sodalite by simulated Hanford tank waste and its impact on cesium retention. *Clays and Clay Minerals*. 2004;52(1):1-13.

169. Rios, C.A., Williams, C.D., Fullen, M.A. Nucleation and growth history of zeolite LTA synthesized from kaolinite by two different methods. *Applied Clay Science*. 2009;42(3-4):446-454.

170. Ríos, C.A., Williams, C.D., Castellanos, O.M. Crystallization of low silica Na-A and Na-X zeolites from transformation of kaolin and obsidian by alkaline fusion. *Ingeniería y Competitividad*. 2012;14(2):125-137.

171. Ma, Y., Yan, C., Alshameri, A., Qiu, X., Zhou, C. Synthesis and characterization of 13X zeolite from low-grade natural kaolin. *Advanced Powder Technology*. 2014;25(2):495-499.

172. Querol, X., Umaña, J.C., Plana, F., Alastuey, A., Lopez-Soler, A., Medinaceli, A., Valero, A., Domingo, M.J. and Garcia-Rojo, E. Synthesis of zeolites from fly ash at pilot plant scale. Examples of potential applications. *Fuel*. 2001;80(6):857-865.

173. Querol, X., Umaña, J.C., Plana, F., Alastuey, A., Lopez-Soler, A., Medinaceli, A., Valero, A., Domingo, M.J. and Garcia-Rojo, E. Synthesis of zeolites from fly ash at pilot plant scale. *Fly-ash Inform*.1999;11-89.

174. Querol, X., Umaña, J.C., Plana, F., Alastuey, A., Lopez-Soler, A., Medinaceli, A., Valero, A., Domingo, M.J. and Garcia-Rojo, E. Synthesis of high ion exchange zeolites from coal fly ash. *Geologica Acta*. 2007;5(1):0049-0057.

175. Anggoro, D.D., Purbasari, A. The optimization of production zeolite Y catalyst from RHA by response surface methodology. *Reaktor*. 2009;12(3):189-194.

176. Ramli, Z., Listiorini, E., Hamdan, H. Optimization and reactivity study of silica in the synthesis of zeolites from rice husk. *Jurnal Teknologi*. 1996;25(1):27-35.

177. Ajala, A.J. *A Study on Thermal Conductivity of six unexplored Nigerian Clays for possible Refractory and Insulating Materials*, Ph.D. Thesis. Universiti Tun Hussein Onn Malaysia; 2017.

178. James, F., Doremus, R. Ceramic and glass materials: Structure, properties and processing. *Editorial Springer, Nueva York, EUA*. 2008:56-62.

179. Spectra, V. Structure of Kaolinite: A Computer Simulation Study. *Journal of Physical Chemistry B.* 2000;104(39):9210-9217.

180. Gilmore, C. *Materials Science and Engineering Properties.* Nelson Education; 2014.

181. Brigatti, M., Galan, E., Theng, B. Structures and mineralogy of clay minerals. *Developments in Clay Science.* 2006;1:19-86.

182. Rocha, J., Klinowski, J., Adams, J.M. Synthesis of zeolite Na-A from metakaolinite revisited. *Journal of the Chemical Society, Faraday Transactions.* 1991;87(18):3091-3097.

183. Wardle, R., Brindley, G. Crystal-Structures of Pyrophyllite, 1Tc, and of its dehydroxylate. *American Mineralogist.* 1972;57(5-6):732-739.

184. Lazo-Vélez, M.A., Avilés-González, J., Serna-Saldivar, S.O., Temblador-Pérez, M.C. Optimization of wheat sprouting for production of selenium enriched kernels using response surface methodology and desirability function. *LWT-Food Science and Technology*. 2016;65:1080-1086.

185. Montgomery, D.C. *Design and Analysis of Experiments.* John wiley & sons; 2017.

186. Dean, A., Voss, D., Draguljić, D. *Design and Analysis of Experiments.* Vol 1: Springer; 1999.

187. Montgomery, D.C. *Design and Analysis of Experiments.* Wiley New York; 1996.

188. He, Z., Zhu, P.F., Park, S.H. A robust desirability function method for multi-response surface optimization considering model uncertainty. *European Journal of Operational Research.* 2012;221(1):241-247.

189. Muhamad, M.H., Abdullah, S.R.S., Mohamad, A.B., Rahman, R.A., Kadhum, A.A.H. Application of response surface methodology (RSM) for optimisation of COD, NH3–N and 2, 4-DCP removal from recycled paper wastewater in a pilot-scale granular activated carbon sequencing batch biofilm reactor (GAC-SBBR). *Journal of Environmental Management.* 2013;121:179-190.

190. Triveni, R., Shamala, T., Rastogi, N. Optimised production and utilisation of exopolysaccharide from Agrobacterium radiobacter. *Process Biochemistry.* 2001;36(8-9):787-795.

191. Aghili, F., Ghoreyshi, A.A., Rahimpour, A., Rahimnejad, M. Coating of mixed-matrix membranes with powdered activated carbon for fouling control and treatment of dairy effluent. *Process Safety and Environmental Protection.* 2017;107:528-539.

192. Malik, A., Grohmann, E., Akhtar, R. *Environmental Deterioration and Human Health: Natural and Anthropogenic Determinants.* Springer Science & Business Media; 2013.

193. Ghosh, P., Kumar, R., Samanta, A., Ray, S. Decontamination of tannery industry wastewater containing high organic load along with Cr_3^+: a

comparative study. *Asia-Pacific Journal of Chemical Engineering.* 2013;8(5):645-656.

194. Ayele, L., Pérez, E., Mayoral, Á., Chebude, Y., Díaz, I. Synthesis of zeolite A using raw kaolin from Ethiopia and its application in removal of Cr (III) from tannery wastewater. *Journal of Chemical Technology & Biotechnology.* 2018;93(1):146-154.

195. Gupta, V., Carrott, P., Ribeiro Carrott, M. Low-cost adsorbents: growing approach to wastewater treatment—a review. *Critical Reviews in Environmental Science and Technology.* 2009;39(10):783-842.

196. Mayoral, A., Carey, T., Anderson, P.A., Diaz, I. Atomic resolution analysis of porous solids: a detailed study of silver ion-exchanged zeolite A. *Microporous and Mesoporous Materials.* 2013;166:117-122.

197. Zollinger, H. *Color Chemistry: Syntheses, Properties, and Applications of Organic Dyes and Pigments.* John Wiley & Sons; 2003.

198. El Haggar, S. *Sustainable industrial design and waste management: cradle-to-cradle for sustainable development.* Academic Press; 2010.

199 Elmoubarki, R., Mahjoubi, F., Tounsadi, H., Moustadraf, J., Abdennouri, M., Zouhri, A. et al. Adsorption of textile dyes on raw and decanted Moroccan clays: Kinetics, equilibrium and thermodynamics. *Water Resources and Industry*. 2015; 9: 16-29.

200 Wei, W., Yang, L., Zhong, W., Li, S., Cui, J., Wei, Z. Fast removal of methylene blue from aqueous solution by adsorption onto poorly crystalline hydroxyapatite nanoparticles. *Digest Journal of Nanomaterials Biostructures*. 2015;19:1343-1363.

201 Jabli, M., Hamdaoui, M., Jabli, A., Ghandour, Y., Ben Hassine, B. A comparative study on the performance of dye removal, from aqueous suspension, using (2-hydroxypropyl)-β-cyclodextrin-CS, PVP-PVA-CS, PVA-CS, PVP-CS and plain CS microspheres. *The Journal of The Textile Institute*. 2014;105:661-675.

202 Hao, J., Kim, H. Chiang, P.C. Decolorization of wastewater. *Critical Reviews in Environmental Science and Technology*. 2000;30:449-505.

203 Gupta, N., Kushwaha, A.K., Chattopadhyaya, M. Adsorption studies of cationic dyes onto Ashoka (Saraca asoca) leaf powder. Journal of the Taiwan Institute of Chemical Engineers. 2012;43:604-613.

204. Foo, K.Y., Hameed, B.H. Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal.* 2010;156(1):2-10.

205. Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society.* 1918;40(9):1361-1403.

206. Mojiri, A., Ziyang, L., Tajuddin, R.M., Farraji, H., Alifar, N. Co-treatment of landfill leachate and municipal wastewater using the ZELIAC/zeolite constructed wetland system. *Journal of Environmental Management.* 2016;166:124-130.

207. Ho, Y., McKay, G. Application of kinetic models to the sorption of copper (II) on to peat. *Adsorption Science & Technology*. 2002;20(8):797-815.

208. Halim, A.A., Abidin, N.N.Z., Awang, N., Ithnin, A., Othman, M.S., Wahab, M.I. Ammonia and COD removal from synthetic leachate using rice husk composite adsorbent. *Journal of Urban and Environmental Engineering.* 2011;5(1):24-31.

209. Freundlich, F. Physikalische Chemie. *Leipzig 57 (1906).* 1906;385.

210. Pikaar, I., Koelmans, A.A., van Noort, P.C. Sorption of organic compounds to activated carbons. Evaluation of isotherm models. *Chemosphere.* 2006;65(11):2343-2351.

211. Zendelska, A., Golomeova, M., Blažev, K., Krstev, B., Golomeov, B., Krstev, A. Kinetic studies of zinc ions removal from aqueous solution by adsorption on natural zeolite. *International Journal of Science, Environment and Technology*. 2014;3(4):1303-1318.

212. Zamora-Villafranco, E, Barceló-Quintal, I.D., Gomez-Salazar, S., Barceló-Quintal, M., Solís-Correa, H.E., Soriano-Rodríguez, J.M. Adsorption kinetics of matter contained in a leachate using eggshell and activated carbon. *Journal of Environmental Protection.* 2014;5(07):608.

213. Weber, W.J., Morris, J.C. Kinetics of adsorption on carbon from solution. *Journal of the Sanitary Engineering Division.* 1963;89(2):31-60.

214. Ho, Y.S. Review of second-order models for adsorption systems. *Journal of Hazardous Materials.* 2006;136(3):681-689.

215. Halim, A.A., Aziz, H.A., Johari, M.A.M., Ariffin, K.S. Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment. *Desalination.* 2010;262(1-3):31-35.

216. Igwe, J., Abia, A. Adsorption kinetics and intraparticulate diffusivities for bioremediation of Co (II), Fe (II) and Cu (II) ions from waste water using modified and unmodified maize cob. *International Journal of Physical Sciences.* 2007;2(5):119-127.

217. Gómez, M. Síntesis, caracterización y aplicaciones catalíticas de zeolitas básicas. *Memoria presentada para optar al grado de Doctor en Ciencias Químicas Facultad de Ciencias Químicas Departamento de Ingeniería Química, Universidad Complutense de Madrid, España.* 2001.

218. Mukasa-Tebandeke, I.Z., Ssebuwufu, P.J.M., Nyanzi, S.A., Schumann, A., Nyakairu, G.W.A., Ntale, M. and Lugolobi, F. The elemental, mineralogical, IR, DTA and XRD analyses characterized clays and clay minerals of Central and Eastern Uganda. 2015.

219. Aydın Temel, F., Kuleyin, A. Ammonium removal from landfill leachate using natural zeolite: kinetic, equilibrium, and thermodynamic studies. *Desalination and Water Treatment.* 2016;57(50):23873-23892.

220. Chen, H., Rogalski, M.M, Anker, J.N. Advances in functional X-ray imaging techniques and contrast agents. *Physical Chemistry Chemical Physics.* 2012;14(39):13469-13486.

221. Islam, M.A., Alam, M.R., Hannan, M.O. Multiresponse optimization based on statistical response surface methodology and desirability function for the production of particleboard. *Composites Part B: Engineering.* 2012;43(3):861-868.

222. Yan, W., Li, N., Li, Y., Liu, G., Han, B., Xu, J. Effect of particle size on microstructure and strength of porous spinel ceramics prepared by pore-forming in situ technique. *Bulletin of Materials Science.* 2011;34(5):1109-1112.

223. Bala, H., Dymek, M., Drulis, H. Development of metal hydride material efficient surface in conditions of galvanostatic charge/discharge cycling. *Materials Chemistry and Physics.* 2014;148(3):1008-1012.

224. Ariffin, K.S., Rahman, H.A., Hussin, H., Hadi, K.A.A. The genesis and characteristics of primary kaolinitic clay occurrence at Bukit Lampas, Simpang Pulai, Ipoh. *Bulletin of the Geological Society of Malaysia.* 2008; 54: 9 – 16.

225. Belviso, C., Cavalcante, F., Lettino, A., Fiore, S. A and X-type zeolites synthesised from kaolinite at low temperature. *Applied Clay Science.* 2013;80:162-168.

226. Ajayi, O., Adefila, S., Ityokumbul, M. Monitoring zeolite NaY formation from potassium-rich Nigerian kaolinite clay. *Ain Shams Engineering Journal.* 2017.

227. El-Diadamony, H., Amer, A.A., Sokkary, T.M., El-Hoseny, S. Hydration and characteristics of metakaolin pozzolanic cement pastes. *HBRC Journal.* 2016.

228. Ilić, B.R., Mitrović, A.A., Miličić, L.R. Thermal treatment of kaolin clay to obtain metakaolin. *Hemijska Industrija.* 2010;64(4):351-356.

229. Yang, N., Zhang, Z.C., Ma, N., Liu, H.L., Zhan, X.Q., Li, B., Gao, W., Tsai, F.C., Jiang, T., Chang, C.J. and Chiang, T.C. Effect of surface modified kaolin on properties of polypropylene grafted maleic anhydride. *Results in Physics.* 2017;7:969-974.

230. Loiola, A., Andrade, J., Sasaki, J., Da Silva, L. Structural analysis of zeolite NaA synthesized by a cost-effective hydrothermal method using kaolin and its use as water softener. *Journal of Colloid and Interface Science.* 2012;367(1):34-39.

231. Musyoka, N.M., Petrik, L.F., Fatoba, O.O., Hums, E. Synthesis of zeolites from coal fly ash using mine waters. *Minerals Engineering.* 2013;53:9-15.

232. Cilla, M.S., de Melo, J., Menezes, R.R., deLima Santana, L.N., de Araujo, G. Production of fire clay porous structure with no aligned macro porosity from water-based slurry by freeze casting process: A new approach. *Ceramics International.* 2016;42(7):9278-9282.

233. Bahng, M.K., Mukarakate, C., Robichaud, D.J., Nimlos, M.R. Current technologies for analysis of biomass thermochemical processing: A review. *Analytica Chimica Acta.* 2009;651(2):117-138.

234. Kubiliūtė, R., Kaminskas, R. The Pozzolanic Activity of Calcined Clay–Silica Gel Composites. *Materials Science.* 2013;19(4):453-460.

235. Liu, H., Shen, T., Li, T., Yuan, P., Shi, G., Bao, X. Green synthesis of zeolites from a natural aluminosilicate mineral rectorite: effects of thermal treatment temperature. *Applied Clay Science.* 2014;90:53-60.

236. Kugbe, J., Matsue, N., Henmi, T. Synthesis of Linde type A zeolite–goethite nanocomposite as an adsorbent for cationic and anionic pollutants. *Journal of Hazardous Materials.* 2009;164(2):929-935.

237. Treacy, M.M., Higgins, J.B. *Collection of Simulated XRD Powder Patterns for Zeolites fifth (5th) revised edition.* Elsevier; 2007.

238. Daneshpayeh, S., Ghasemi, F.A., Ghasemi, I., Ayaz, M. Predicting of mechanical properties of PP/LLDPE/TiO2 nano-composites by response surface methodology. *Composites Part B: Engineering.* 2016;84:109-120.

239. Mizutani, N., Iwasaki, T., Watano, S. Response surface methodology study on magnetite nanoparticle formation under hydrothermal conditions. *Nanomaterials and Nanotechnology*. 2015;5-13.

240. Heller-Kallai, L., Lapides, I. Reactions of kaolinites and metakaolinites with NaOH—comparison of different samples (Part 1). *Applied Clay Science.* 2007;35(1-2):99-107.

241. Chandrasekhar, S., Pramada, P. Kaolin-based zeolite Y, a precursor for cordierite ceramics. *Applied Clay Science.* 2004;27(3-4):187-198.

242. Costa, E., De Lucas, A., Uguina, M.A., Ruiz, J.C. Synthesis of 4A zeolite from calcined kaolins for use in detergents. *Industrial & engineering chemistry research.* 1988;27(7):1291-1296.

243. Belviso, C., Giannossa, L.C., Huertas, F.J., Lettino, A., Mangone, A., Fiore, S. Synthesis of zeolites at low temperatures in fly ash-kaolinite mixtures. *Microporous and Mesoporous Materials.* 2015;212:35-47.

244. Li, Y., Yang, W. Microwave synthesis of zeolite membranes: a review. *Journal of Membrane Science.* 2008;316(1-2):3-17.

245. Wakihara, T., Sugiyama, A., Okubo, T. Crystal growth of faujasite observed by atomic force microscopy. *Microporous and Mesoporous Materials.* 2004;70(1-3):7-13.

246. Han, Y., Ma, H., Qiu, S., Xiao, F.S. Preparation of zeolite A membranes by microwave heating. *Microporous and Mesoporous Materials.* 1999;30(2-3):321-326.

247. Du, C., Yang, H. Synthesis and characterization of zeolite 4A-type desiccant from kaolin. *American Mineralogist.* 2010;95(5-6):741-746.

248. Bonaccorsi, L., Proverbio, E. Microwave assisted crystallization of zeolite A from dense gels. *Journal of Crystal Growth.* 2003;247(3-4):555-562.

249. Počkaj, M., Meden, A., Logar, N.Z., Rangus, M., Mali, G., Lezcano-Gonzalez, I., Beale, A.M. and Golobič, A. Structural investigations in pure-silica and Al-ZSM-12 with MTEA or TEA cations. *Microporous and Mesoporous Materials.* 2018;263:236-242.

250. Psycharis, V., Perdikatsis, V., Christidis, G. Crystal structure and Rietveld refinement of zeolite A synthesized from fine-grained perlite waste materials. *Bulletin of the Geological Society of Greece.* 2004;36(1):121-129.

251. Matsumoto, M., Takahashi, M., Hirata, M., Ono, A., Hirose, A. From OECD High Production Quantity Chemical Inspection Program to OECD Chemical Entity Joint Evaluation Program. *Chemistry Biological Management* 2012;8(2):173-233.

252. Kaiser, R., Kulczyk, A., Rich, D., Willey, R.J., Minicucci, J., MacIver, B. Effect of pore size distribution of commercial activated carbon fabrics on the adsorption of CWA simulants from the liquid phase. *Industrial & Engineering Chemistry Research.* 2007;46(19):6126-6132.

253. Santos, S.C., Boaventura, R.A. Adsorption of cationic and anionic azo dyes on sepiolite clay: equilibrium and kinetic studies in batch mode. *Journal of Environmental Chemical Engineering*. 2016;4(2):1473-1483.

254. Werkneh, A.A., Habtu, N.G., Beyene, H.D. Removal of hexavalent chromium from tannery wastewater using activated carbon primed from sugarcane bagasse: Adsorption/desorption studies. *American Journal of Applied Chemistry*. 2014;2(6):128-135.

255. Banerjee, S., Sharma, Y.C. Equilibrium and kinetic studies for removal of malachite green from aqueous solution by a low cost activated carbon. *Journal of Industrial and Engineering Chemistry.* 2013;19(4):1099-1105.

256. Çelekli, A., İlgün, G., Bozkurt, H. Sorption equilibrium, kinetic, thermodynamic, and desorption studies of Reactive Red 120 on Chara contraria. *Chemical Engineering Journal*. 2012;191:228-235.

257. Ghaedi, M., Sadeghian, B., Pebdani, A.A., Sahraei, R., Daneshfar, A., Duran, C. Kinetics, thermodynamics and equilibrium evaluation of direct yellow 12 removal by adsorption onto silver nanoparticles loaded activated carbon. *Chemical Engineering Journal.* 2012;187:133-141.

258. Sharma, Y., Upadhyay, U.S., Gode, F. Adsorptive removal of a basic dye from water and wastewater by activated carbon. *J of Applied Science in Environmental Sanitation.* 2009;4:21-24.

259. Erdem, E., Karapinar, N., Donat, R. The removal of heavy metal cations by natural zeolites. *Journal of Colloid and Interface Science.* 2004;280(2):309-314.

260. Hameed, B., Ahmad, A., Aziz, N. Adsorption of reactive dye on palm-oil industry waste: equilibrium, kinetic and thermodynamic studies. *Desalination.* 2009;247(1-3):551-560.

261. Han, Z.X., Zhu, Z., Wu, D.D,, Wu, J., Liu, Y.R. Adsorption kinetics and thermodynamics of acid blue 25 and methylene blue dye solutions on natural sepiolite. *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*. 2014;44(1):140-147.

262. Tümsek, F., Avcı, O. Investigation of kinetics and isotherm models for the acid orange 95 adsorption from aqueous solution onto natural minerals. *Journal of Chemical & Engineering Data.* 2013;58(3):551-559.

263. Tabak, A., Eren, E., Afsin, B., Caglar, B. Determination of adsorptive properties of a Turkish Sepiolite for removal of Reactive Blue 15 anionic dye from aqueous solutions. *Journal of Hazardous Materials.* 2009;161(2-3):1087-1094.

264. El-Gammal, B., Metwally, S., Aly, H., Abo-El-Enein, S. Verification of double-shell model for sorption of cesium, cobalt, and europium ions on poly-acrylonitrile-based Ce (IV) phosphate from aqueous solutions. *Desalination and Water Treatment.* 2012;46(1-3):124-138.

265. Elmoubarki, R., Mahjoubi, F., Tounsadi, H. Adsorption of textile dyes on raw and decanted Moroccan clays: Kinetics, equilibrium and thermodynamics. *Water Resources and Industry.* 2015;9:16-29.

266. Praveen, P., Loh, K.C. Solventless extraction/stripping of phenol using trioctylphosphine oxide impregnated hollow fiber membranes–Experimental & modeling analysis. *Chemical Engineering Journal.* 2014;255:641-649.

267. De Gisi, S., Lofrano, G., Grassi, M., Notarnicola, M. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: a review. *Sustainable Materials and Technologies.* 2016;9:10-40.

268. Sehweil, S. *Wastewater Reuse for Irrigation Purposes on Soil Conditioned with Zeolite*, Birzeit University; 2013.

269. Ahmadi, S., Kord Mostafapour, S. Tea waste as a low cost adsorbent for the removal of COD from landfill leachate: Kinetic Study. *Journal of Science Engineering Resources.* 2017;4(6):103-108.

270. Khan, T.A., Khan, E.A. Removal of basic dyes from aqueous solution by adsorption onto binary iron-manganese oxide coated kaolinite: Non-linear isotherm and kinetics modeling. *Applied Clay Science.* 2015;107:70-77.

271. Senthil Kumar, P., Fernando, P.S.A., Ahmed, R.T., Srinath, R., Priyadharshini, M., Vignesh, A.M. and Thanjiappan, A. Effect of temperature on the adsorption of methylene blue dye onto sulfuric acid–treated orange peel. *Chemical Engineering Communications.* 2014;201(11):1526-1547.

272. Demir, A., Gunay, A., Debik, E. Ammonium removal from aqueous solution by ion-exchange using packed bed natural zeolite. *Water SA.* 2002;28(3):329-336.

273. Du, Q., Liu, S., Cao, Z., Wang, Y. Ammonia removal from aqueous solution using natural Chinese clinoptilolite. *Separation and Purification Technology.* 2005;44(3):229-234.

274. Widiastuti, N., Wu, H., Ang, H.M., Zhang, D. Removal of ammonium from greywater using natural zeolite. *Desalination.* 2011;277(1-3):15-23.

275. Khamidun, M.H., Fulazzaky, M.A. Adsorption of phosphate from synthetic solution onto the limestone in a plug-flow column. *International Journal of Advanced and Applied Sciences.* 2015;2(12):7-13.

271. Foul, A.A., Aziz, H.A., Isa, M.H., Hung, Y.T. Primary treatment of anaerobic landfill leachate using activated carbon and limestone: batch and column studies. *International Journal of Environment and Waste Management.* 2009;4(3-4):282-298.

276. Rao, V.B., Rao, S.R.M. Adsorption studies on treatment of textile dyeing industrial effluent by flyash. *Chemical Engineering Journal*. 2006;116(1):77-84.

277. Li, C.F., Ge, X.L., Liu, S.G., Liu, F.Y. Synthesis of Novel Core-Shell Structured Hydroxyapatite/Meso-Silica for Removal of Methylene Blue from Aqueous Solutions. Paper presented at: *Advanced Materials Research*, 2012.

278. Sharma, Y.C., Upadhyay, S.N. Removal of a cationic dye from wastewaters by adsorption on activated carbon developed from coconut coir. *Energy & Fuels*. 2009;23(6):2983-2988.

279. Khanday, W.A., Majid, S.A., Shekar, S.C, Tomar, R. Dynamic adsorption of DMMP over synthetic zeolite-Alpha. *Arabian Journal of Chemistry*. 2014;7(1):115-123.

280. Pirbazari, A.E., Saberikhah, E., Kozani, S.H. Fe_3O_4–wheat straw: preparation, characterization and its application for methylene blue adsorption. *Water Resources and Industry*. 2014;7:23-37.

281. Sarioglu, M. Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite. *Separation and Purification Technology*. 2005;41(1):1-11.

282. Leyva-Ramos, R., Aguilar-Armenta, G., Gonzalez-Gutierrez, LV., Guerrero-Coronado, R.M., Mendoza-Barron, J. Ammonia exchange on clinoptilolite from mineral deposits located in Mexico. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*. 2004;79(6):651-657.